SYNTHESIS OF SUPERCHARGED CHITOSAN DERIVATIVES

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Relevance: Modern polymer chemistry is actively evolving toward the development of functionalized biopolymers with tailored physicochemical and biomedical properties. Chitosan, a derivative of chitin, is a polymer containing reactive amino groups, which makes it a promising raw material for the design of novel biologically active macromolecular systems. One of the key requirements for chitosan derivatives is their solubility under neutral or mildly alkaline conditions. However, the limited solubility of native chitosan significantly restricts its practical applications. Therefore, the development of highly charged chitosan derivatives remains a relevant and promising research direction. In this context, the introduction of cationic groups into the chitosan backbone can enhance not only its solubility at neutral or slightly alkaline pH values but also its inherent biological activity.

Purpose of the study: Synthesis of Supercharged Chitosan Derivatives Exhibiting Diverse Physicochemical Characteristics.

Materials and methods: 1 g of chitosan hydrochloride (molecular weight 230.0 kDa, degree of deacetylation 85%) was dispersed in 100 mL of ethanol and allowed to swell for 2 hours. After swelling, a low-molecular-weight reagent was added at a molar ratio of chitosan to cyanoguanidine = 1:1-4. The reaction mixture was stirred for 5-10 hours at 60-80°C. Upon completion, the precipitate formed was separated by decantation, dissolved in 1% hydrochloric acid, and reprecipitated with acetone. The resulting solid was redissolved in water and purified by dialysis for 48 hours, with five changes of dialysis water. Finally, the purified product was subjected to lyophilization and analyzed.

Results: Upon reaction of cyanoguanidine with the amino groups of chitosan, a nucleophilic addition occurs, leading to the formation of guanidinium moieties. The conducted studies demonstrated that by varying the reaction conditions specifically the molar ratio of reactants, reaction time, and temperature it is possible to obtain chitosan derivatives with a degree of substitution ranging from 0.15 to 0.64 mol%. The presence of guanidinium groups in the chitosan backbone was confirmed by FTIR and NMR spectroscopy. Introduction of guanidinium fragments into the macromolecular chain significantly improved the solubility of chitosan across a wide pH range. While native chitosan is insoluble in neutral and alkaline media, the synthesized derivatives remained soluble within the pH range of 3 to 9.

In addition, the included guanidine groups increased the overall charge of chitosan (38 mV) and the ζ-potential value was 45-58 mV.This increase in positive charge may have a direct impact on the physiological properties of chitosan. For instance, stronger electrostatic interactions with cell membranes could enhance both its antimicrobial activity and its cell adhesion capacity, thereby broadening the potential biomedical applications of guanidinium-functionalized chitosan.

Conclusions: Thus, the synthesized supercharged chitosan derivatives containing guanidinium groups exhibit improved physicochemical characteristics, including an expanded solubility range and

an increased positive surface charge. These properties indicate the potential of the modified chitosan derivatives for use in various biomedical applications.

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